REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response; including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completting and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Hedquarters Services. Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 222024302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.						
1. AGENCY USE ONLY (Leave					AND DATES COVERED	
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Colloid Inter-Comparison Exercise - The Colloid "Cookout"					N00014-94-1-0633	
6. AUTHOR(S)					1	
Dr. Ken O. Buesseler						
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)					8 PF	REFORMING ORGANIZATION
Woods Hole Oceanographic Institution					REPORT NUMBER	
360 Woods Hole Rd.						
MS-25 Woods Hole, MA 02543-1541					G (	E IIIVA
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)					10 SP	ONSORING/MONITORING
Office of Naval Research					1.40	ENGE BEPPRTINGINGER
Ballston Towers One						
800 North Quincy Street Arlington, VA 22217						
11. SUPPLEMENTARY NOTES						
12a. DISTRIBUTION / AVAILABILITY STATEMENT						
UNLIMITED DISTRIBUTION STATEMENT A					UL.	
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13. ABSTRACT (Maximum 200 wo	rds)					
With the application of an ever increasing variety of CFF system designs, and the reports of spatial and seasonal differences in the abundance and composition of marine colloids (e.g. Baskaran et al., 1992; Moran and Buesseler, 1993), it was clear that a careful evaluation of the performance of currently available CFF technologies was needed. To begin this assessment, we conducted an intercomparison study of CFF for the isolation of marine colloids from seawater. Thirteen different groups gathered first at the Woods Hole Oceanographic Institution and later at the National Energy Laboratory of Hawaii to process simultaneously common seawater samples with their CFF systems. The goal of this study was to assess quantitatively whether ultrafiltration systems from different manufacturer's and used under different operating conditions provided results which were reasonably consistent in both nearshore and offshore environments.  15. Number of Pages  16. PRICE CODE						
7. SECURITY CLASSIFICATION OF REPORT		URITY CLASSIFICATION THIS PAGE	19. S	ECURITY CLASSIFICA OF ABSTRACT	TION	20. LIMITATION OF ABSTRACT
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Standard Form 298 (Rev. 2-89) Prescribed by ANSI Std. 239-18 298-102

# COLLOID INTER-COMPARISON EXERCISE- THE COLLOID "COOKOUT" Final Report - ONR Grant #N00014-94-1-0633

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#### RESEARCH GOALS:

An intercomparison was conducted between 14 cross-flow filtration (CFF) systems for their ability to isolate marine colloids from seawater. The goal of this exercise was to examine if the different CFF systems were behaving in a well defined and operationally reproducible and consistent manner.

#### **OBJECTIVES:**

With the application of an ever increasing variety of CFF system designs, and the reports of spatial and seasonal differences in the abundance and composition of marine colloids (e.g. Baskaran et al., 1992; Moran and Buesseler, 1993), it was clear that a careful evaluation of the performance of currently available CFF technologies was needed. To begin this assessment, we conducted an intercomparison study of CFF for the isolation of marine colloids from seawater. Thirteen different groups gathered first at the Woods Hole Oceanographic Institution and later at the National Energy Laboratory of Hawaii to process simultaneously common seawater samples with their CFF systems. The goal of this study was to assess quantitatively whether ultrafiltration systems from different manufacturer's and used under different operating conditions provided results which were reasonably consistent in both nearshore and offshore environments.

#### APPROACH:

Surface seawater from a coastal site and mid-ocean waters from an open ocean site were prefiltered (<0.2 µm) and subsamples were processed according to individual protocols with each group using a 1,000 NMW CFF membrane. The main criterion for this intercomparison was the bulk organic carbon (OC) content of the dissolved and colloidal fractions. Since colloids are proposed to be important intermediaries in the cycling of many particle-reactive trace metals, so we also examined the behavior of two trace metals, Al and Fe, as part of the intercomparison (Reitmeyer et al., 1995). Cd, Cu and Ni were also examined on a selected set of samples (Greenamoyer and Moran, 1995) and ICPMS trace metal analyses were conducted on a colloid fraction from a single CFF system (Bertine and VernonClark, 1995). Other analyses of the intercomparison samples included absorbence and fluorescence spectra (Feng et al., 1995), nutrients, DON and DOP (Bauer et al., 1995), as well as one tracer experiment conducted with a standard macromolecule of known size which was added to seawater and processed similar to the samples (Gustafsson et al., 1995).

### TASKS COMPLETED:

In 1995, we conducted our second intercomparison experiment at the NELH facility in Hawaii. We also conducted a short meeting at this site, related to the results from our sampling in Aug. 1994 in Woods Hole. All groups were invited to submit manuscripts on their results by Sept. 1, 1995, for a special issue of Marine Chemistry that is being guest edited by the PI from this project (a complete list of submitted papers is provided below).

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The results suggest that there are large differences in the quantity of colloidal material isolated by standard CFF systems, depending upon the specific membrane used, and to some extent, the operating protocols. At present, the consistency of results between samples within any single system is good. However, even between nearly identical systems from the same manufacturer, the variability in the quantity of colloidal OC isolated increases to a factor of 5 or more. Even greater differences were to be found between different manufacturer's CFF systems. For example, using the Amicon 1,000 NMW systems we found relatively high colloidal OC abundances in the intermediate waters off Hawaii (>15 to 70%), whereas, with any of the other CFF system, we detected essentially no colloidal OC in these same samples (<2%).

We were not able to reach a consensus as to a single system that could be recommended for all users, although some systems seemed to be plagued with generally higher OC blanks and low retention relative to the membrane's rated cut-off. Within a single group of systems, there were clearly operational practices that improved performance and minimized blanks and other obvious artifacts. We have some indication that the composition of the colloidal material also varied amongst CFF systems, so fractionation is considered likely, at least with respect to trace constituents with differing chemical properties. Time-series sampling demonstrated that variations in permeate concentration need to be considered.

#### SCIENTIFIC ACCOMPLISHMENTS:

Cross-flow filtration will continue to be used in marine studies as it remains the only practical method for processing large volume samples in order to extract colloidal material for chemical analyses or biological experimentation. Given the results of this intercomparison some caution is in order. Work must continue to better characterize the properties of a single or set of CFF systems, before they are more broadly applied in oceanographic studies (Gustafsson *et al.*, 1995; Guo and Santschi, 1995). Careful studies with standard compounds in seawater media and permeation models applicable to natural compound assemblages are needed. Future studies are also needed to determine the effect of manipulating operating parameters on the separation process.

REFERENCES- other than those listed below from the *Marine Chemistry* volume:

- Baskaran, M., Santschi, P.H., Benoit, G. and Honeyman, B.D., 1992. Scavenging of Thorium Isotopes by Colloids in Seawater of the Gulf of Mexico. *Geochim. Cosmochim. Acta*, 56: 3375-3388.
- Moran, S.B. and Buesseler, K.O., 1993. Size-Fractionated <sup>234</sup>Th in Continental Shelf Waters off New England: Implications for the Role of Colloids in Oceanic Trace Metal Scavenging. *J. Mar. Res.*, **51**: 893-922.

REFERENCES- complete list of papers submitted to *Marine Chemistry* volume (K. Buesseler, guest editor).

- Bauer, J. E., Ruttenberg, K. C., Wolgast, D. M., Monaghan, E., and Schrope, M. K., 1995. Dissolved and Colloidal Nitrogen and Phosphorous Isolated from Seawater Using Different Cross-Flow Filtration Technologies. *Mar. Chem.*, submitted.
- Bertine, K. K., and VernonClark, R., 1995. Elemental Composition of Colloidal Phase in WHOI Seawater Sample. *Mar. Chem.*, submitted.

- Buesseler, K. O., Bauer, J. E., Chen, R. F., Eglinton, T. I., Gustafsson, O., Landing, W., Mopper, K., Moran, S.B., Santschi, P. H., VernonClark, R., and Wells, M. L., 1995. Sampling Marine Colloids Using Cross-Flow Filtration: Overview and Results from an Intercomparison Study. *Mar. Chem.*, submitted.
- Greenamoyer, J.M. and Moran, S.B., 1995. Evaluation of a Spiral Wound Cross-Flow Filtration System for Submicron Sampling of Cd, Cu and Ni in Seawater. *Mar. Chem.*, submitted.
- Guentzel, J. L., Powell, R. T., Landing, W. M., and Mason, R. P., 1995. Preliminary Observations of Colloidal Mercury in an Estuarine and Remote Open Ocean Environment. *Mar. Chem.*, submitted.
- Guo, L. and Santschi, P.H., 1995. A Critical Evaluation of the Cross-Flow Ultrafiltration Technique for Sampling of Colloidal Organic Carbon in Seawater. *Mar. Chem.*, submitted.
- Gustafsson, O., Buesseler, K.O. and Gschwend, P.M., 1995. On the Integrity of Cross-Flow Filtration for Marine Organic Colloids. *Mar. Chem.*, submitted.
- Mopper, K., Feng, Z., Bentjen, S. B., and Chen, R. F., 1995. Effects of Cross-Flow Filtration on the Absorption and Fluorescence Properties of Seawater. *Mar. Chem.*, submitted.
- Powell, R. T., Landing, W. M. and Bauer, J. E., 1995. Colloidal Trace Metals, Organic Carbon and Nitrogen in a Southeastern U.S. Estuary. *Mar. Chem.*, submitted.
- Reitmeyer, R., Powell, R. T., Landing, W. M., and Measures, C. I., 1995. Colloidal Al and Fe in Seawater: An Intercomparison between Various Cross-Flow Ultrafiltration Systems. *Mar. Chem.*, submitted.
- Wen, L.-S., Stordal, M.C., Tang, D., Gill, G.A. and Santschi, P.H., 1995. An Ultraclean Cross-Flow Ultrafiltration Technique for the Study of Trace Metal Phase Speciation in Seawater. *Mar. Chem.*, submitted.

## ADDITIONAL INFORMATION RELEVANT TO THIS GRANT OCT. 1, 1993 TO SEPT. 31, 1995

## Manuscripts Submitted by PI:

- Buesseler, K., J. Bauer, R. Chen, T Eglinton, O. Gustafsson, W. Landing, K. Mopper, S. B. Moran, P. Santschi, R. Vernon Clark, M. Wells (1995). Sampling Marine Colloids Using Cross-Flow Filtration: Overview and Results from an Intercomparison Study. *Marine Chemistry*.
- Gustafsson, O., K. O. Buesseler, and P. M. Gschwend (1995). On the Integrity of Cross-Flow Filtration for Marine Organic Colloids. *Marine Chemistry*.

#### Published Abstracts from PI:

Buesseler, K. O., S. B. Moran (1993). In-situ Collection of Marine Colloids and their Thorium Isotopic Signature. American Chemical Society, March 1994 meeting in San Diego.

- Gustafsson, Ö, K. O. Buesseler, S. B. Moran, P. M. Gschwend (1993). Physical Speciation and <sup>234</sup>Th-Derived Transfer Rates of Individual Hydrophobic Compounds in Coastal Seawater. American Chemical Society, submitted for March 1994 meeting in San Diego.
- Moran, S. B. and K. O. Buesseler (1993). Size-Fractionated <sup>234</sup>Th in Seawater: Implications for the Role of Colloids in Oceanic Trace Metal Scavenging. American Chemical Society, March 1994 meeting in San Diego.
- Buesseler, K. O., S. B. Moran, R. L. Edwards, J. A. Hoff, M. C. Hartman, J. E. Andrews, R. A. Belastock, C. R. Benitez (1994). Residence Times of Colloids and Particles Along the Shelf and Slope of the NE USA Derived from Thorium Isotopes. *EOS*, **75**(44), 311.

Invited Talks by PI

Buesseler, K. O. (1995). Recent Advances in Using Thorium-234 as a Tracer of Upper Ocean Particle Export. Invited Speaker: Chemical Oceanography Gordon Research Conference, June 14.

Submitted Abstracts from PI:

Upcoming AGU/ASLO Ocean Sciences meeting-Feb. 1996 in San Diego (all of these three abstracts are now accepted in special session on colloids)

- Buesseler, K.O. (1995) Sampling Marine Colloids using Cross-Flow Filtration: Overview and Results from the "Colloid Cookout" (Invited Speaker)
- Gustafsson, O., K.O. Buesseler and P.M. Gschwend (1995). On the Integrity of Cross-Flow Filtration for Marine Organic Colloids
- Ripple, P., K.O. Buesseler, M. Dai, and J. Andrews (1995). An Evaluation of Two Cross-Flow Filters for their Ability to Isolate Marine Colloids.

FUNDS FROM THIS RESEARCH GRANT WERE USED PRIMARILY TO SUPPORT TRAVEL AND SHIPPING NEEDS OF THE FOLLOWING SCIENTISTS:

#### COLLOID COOKOUT- JAN. 1995 HAWAII PARTICIPANTS LIST:

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Salary funds from this research grant were used by the PI and 3 WHOI support personnel. The following break-down relates to these personnel only, and not those outside of the PI's lab who were supported by this grant for travel and shipping costs related to this project.

Number of undergraduate students supported part time-0
Number of graduate students supported part time-0
Number of post-docs supported part time-0
Number of other technical personnel supported part time-3
Number of female graduate students-0
Number of minority graduate students-0
Number of Asian graduate students-0
Number of female post-docs-0
Number of minority post-docs-0
Number of Asian post-docs-0
Listing of patents filed or granted-0
Listing of awards, honors and prizes with brief description-0.